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<b>14. ABSTRACT</b> <p>The purpose of the research is to study the morphological stability of Ni/Ni<sub>3</sub>Al layered materials, as a function of interfacial orientational relationships, columnar grain dimensions, bilayer thickness, applied stress, and temperature. This report describes our efforts over the past year to model critical features which control the strength of interfaces to dislocation transmission, and to study the morphological stability of Ni(Al)/Ni<sub>3</sub>Al that are heated to elevated temperature for prolonged periods. These two areas are critical to optimizing both the plastic strength and elevated temperature stability of nanoscale materials.</p> <p>This final report describes our efforts to both model the thermal stability of Ni/Ni<sub>3</sub>Al layered materials and to conduct experiments to determine the temperature and time scales over which the layered morphology in such materials may break down.</p>					
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# REPORT OF INVENTIONS AND SUBCONTRACTS

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Anderson, Peter M.	NONE								

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a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, Middle Initial) Peter M. Anderson		b. TITLE Associate Professor		c. SIGNATURE Peter M. Anderson	
				3. DATE SIGNED 06-DEC-01	

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Final Technical Report

1 JUN 97 to 31 MAY 01

**THERMAL STABILITY OF NI(Al)/Ni<sub>3</sub>Al NANOLAYERED MATERIALS**

**GRANT NUMBER: F49620-97-1-0439**

Peter M. Anderson  
Hamish L. Fraser  
Department of Materials Science and Engineering  
Ohio State University

December 10, 2001

**Abstract**

The purpose of this AASERT-sponsored research is to study the morphological stability of Ni(Al)/Ni<sub>3</sub>Al nanoscale layered materials, as a function of interfacial orientational relationships, columnar grain dimensions, bilayer thickness, applied stress, and temperature. This final report describes our efforts over the course of the project to study the morphological stability of Ni(Al)/Ni<sub>3</sub>Al multilayer thin films that are heated to elevated temperature for prolonged periods. This area, when coupled with the objective of the parent project to optimize plastic strength in such materials, represent two critical design areas for nanoscale materials.

This final report describes our efforts to both model the thermal stability of Ni(Al)/Ni<sub>3</sub>Al nanoscale layered materials and to conduct experiments to determine the temperature and time scales over which the layered morphology in such materials may break down.

**Research Objectives**

The research objectives are two-fold. The first is to conduct experiments to determine the morphological stability of Ni(Al)/Ni<sub>3</sub>Al layered materials. The second is to report on existing models of morphological stability and to apply appropriate models to this system.

**Summary of Research Findings and Activities**

**Fabrication of Ni(Al)/Ni<sub>3</sub>Al Multilayer Thin Films**

Multilayer Ni(Al)/Ni<sub>3</sub>Al thin films in free standing, dogbone-shaped geometries were produced by Gregory Thompson and Jason Fain, the supported AASERT students on this project. The fabrication work progressed to the point that, for the first time known to the investigators,  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayers have been produced by magnetron sputtering. Fig. 1 shows the Ultra-High Vacuum magnetron sputtering apparatus used to fabricate the samples. Samples with individual layer thicknesses ranging from 20nm/20nm to 120nm/120nm have been produced and two textures, <001>

and  $\langle 111 \rangle$ , normal to the interfaces have been achieved. A base pressure of  $5 \times 10^{-8}$  torr with a backfilled Argon pressure of  $2 \times 10^{-3}$  torr, and 200W of DC power was used for all samples. A  $\langle 111 \rangle$  texture was achieved by using (100) single crystal Si substrates with a 200nm oxide and deposition temperatures ranging from 200C to room temperature. The same texture was also achieved by using a (100) single crystal NaCl substrate at ambient temperature. A  $\langle 001 \rangle$  texture was obtained by using a (100) single crystal NaCl substrate, but at a deposition temperatures greater than 450C. **Figure 2** shows an example of a  $\langle 001 \rangle$  120nm/120nm multilayer thin film, as produced.



Fig. 1: View of the Ultra-High Vacuum Magnetron Sputtering Apparatus at Ohio State University used to fabricate the Ni(Al)/Ni<sub>3</sub>Al multilayer thin films.

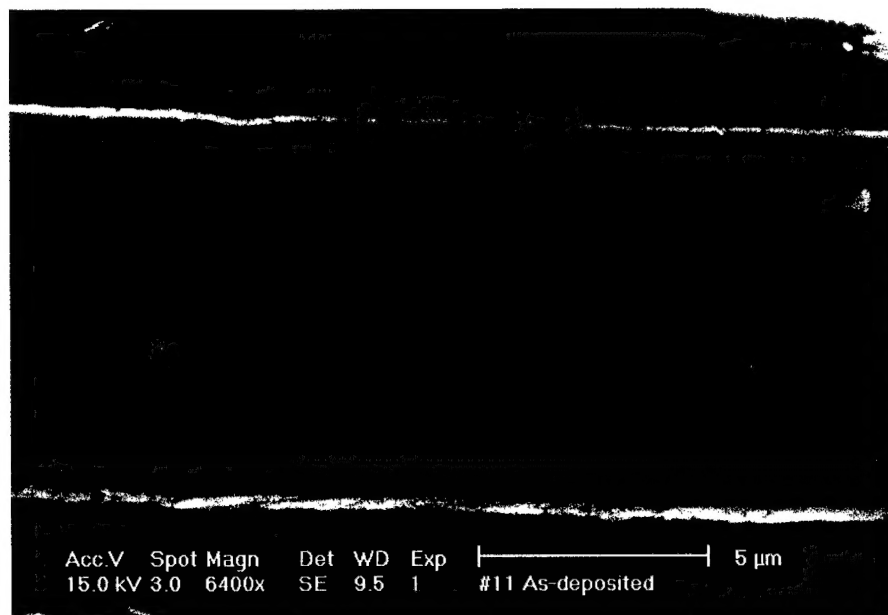


Fig. 2: Cross sectional SEM micrograph of a  $\langle 001 \rangle$  120nm/120nm Ni(Al)/Ni<sub>3</sub>Al multilayer thin film as produced by UHV magnetron sputtering.

*The Effect of Layer Thickness and Texture on the Morphological Stability of Ni(Al)/Ni<sub>3</sub>Al Multilayer Thin Films at 800C for 101 hours*

Figures 3 to 6 display the SEM micrographs of polished  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al samples after heating at 800C for 101 hours in an Argon atmosphere. The results indicate that all multilayers tested show the tendency for layers to pinch off. This is evident in Fig. 3, where layers are pinched off at several locations. An overall comparison reveals that, for a given epitaxy, 20nm/20nm multilayers suffer this instability more rapidly than 120nm/120nm multilayers. Further, the  $\langle 111 \rangle$  epitaxy cases (see Figs. 5 and 6) display a more rapid instability than  $\langle 001 \rangle$  cases with comparable layer thickness (see Figs. 3 and 4). Thus, the  $\langle 001 \rangle$  120nm/120nm case (Fig. 3) was the most resistant to pinching off while the  $\langle 111 \rangle$  20nm/20nm sample (Fig. 6) was the least resistant.

The  $\langle 001 \rangle$  20nm/20nm micrograph (Fig. 4) is unique among those shown, in that morphological breakdown resembles a cuboidal particulate microstructure. Significant coarsening of grains has occurred, since the average particle size is many times the 20nm dimension of the individual layers from which they were produced.

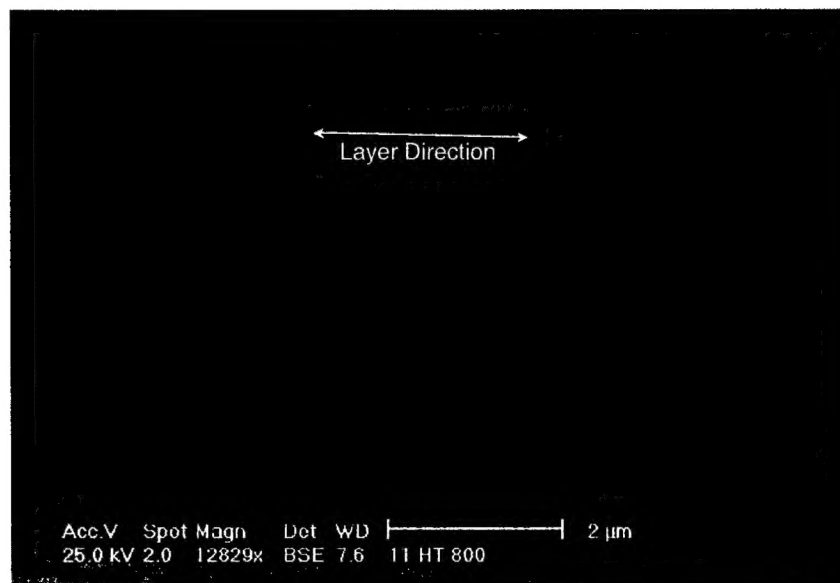


Fig. 3: Morphology of a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 800C for 101 hours in an Argon atmosphere (#11-10). Note the concerted pinching off of several  $\gamma'$  layers along a vertical direction through the multilayer.

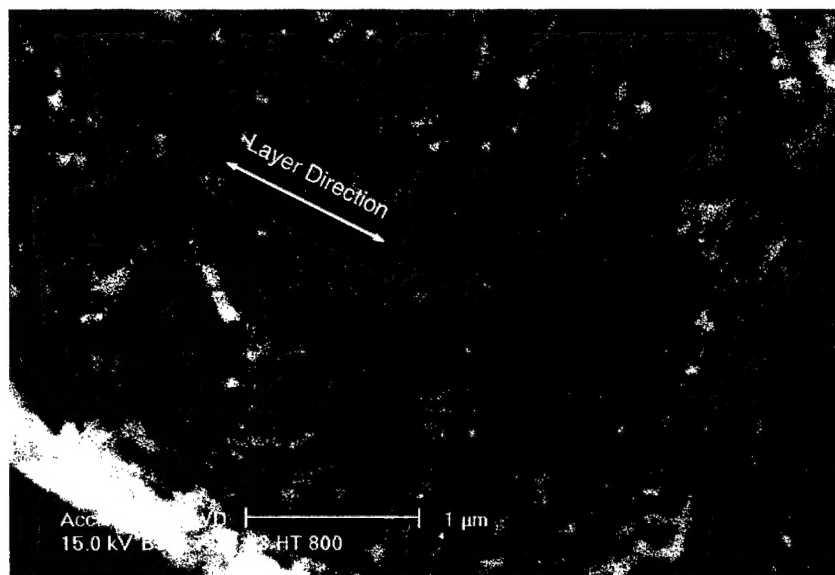


Fig. 4: Morphology of a  $\langle 001 \rangle$  20nm/20nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 800C for 101 hours in an Argon atmosphere (#13-3). Note the particulate morphology forming from the remnants of layers.

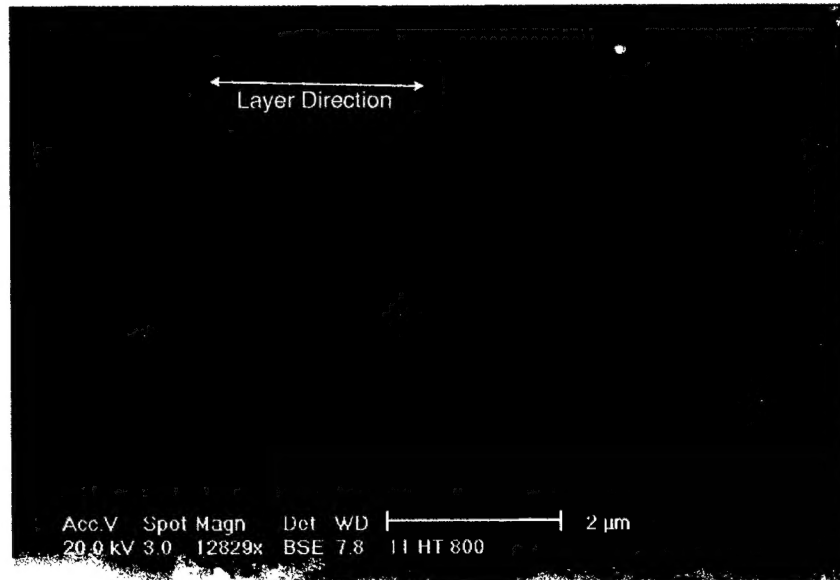


Fig. 5: Morphology of <111> 120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 800C for 101 hours in an Argon atmosphere(#10-4). Note the alignment of particles reminiscent of the layered structure.

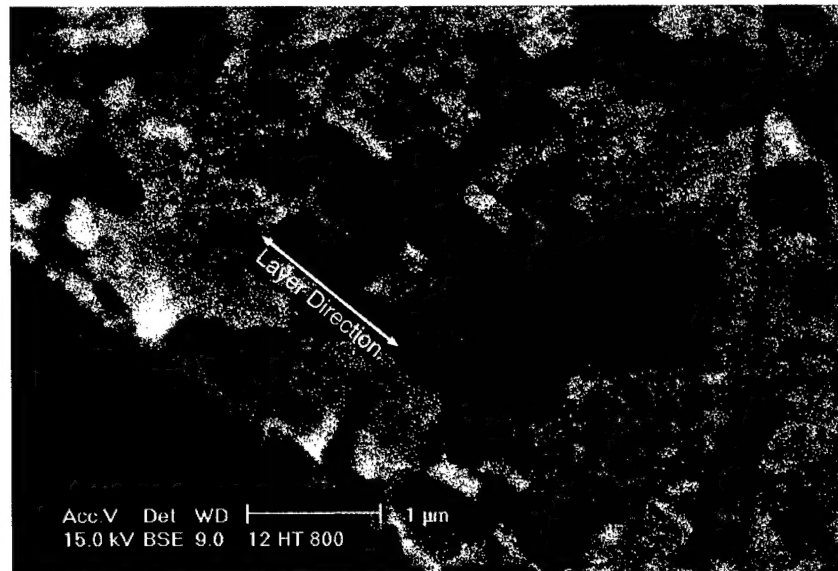


Fig. 6: Morphology of <111> 20nm/20nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 800C for 101 hours in an Argon atmosphere (#12-7). Note that significant coarsening has occurred, since the particles are several time the initial layer thickness.

*The Effect of Elevated Temperature on the Morphology of 120nm/120nm Ni(Al)/Ni<sub>3</sub>Al Multilayer Thin Films with <001> Texture*

The <001> 120nm/120nm multilayers were identified for further study, since they exhibited more resistance to layer breakdown than the 20nm/20nm <001> multilayers and corresponding <111> texture multilayers. Figures 7 to 10 show the different morphologies obtained when 120nm/120nm Ni(Al)/Ni<sub>3</sub>Al multilayers with <001> texture were heated in an Argon atmosphere to different temperatures for 20 hours. Figure 7 clearly shows the pinching off of the Ni<sub>3</sub>Al layers at numerous locations. The columnar microstructure offers numerous locations for pinching off along grain boundaries, but the micrograph indicates a clear preference for pinching off along a subset of grain boundaries. These preferred boundaries appear to be aligned across a large portion of the multilayer. It is unclear whether this concerted pinching off process is a result of the continuation of particular high energy columnar grain boundaries through the multilayer thickness or whether the process is due to a kind of shedding of instability from one pinched off layer to the next. Figure 8 displays results for 900C for 20 hours and has similar features to that for 800C. The co-operative pinching off process through the thickness of the is even more pronounced at this temperature and time, and the strong pinch off locations appear to have a periodic in-plane spacing. Large, multiple-layer regions of Ni(Al) and Ni<sub>3</sub>Al has formed, indicating the onset of coarsening.

Figures 9(a) and (b) show the resulting microstructure after 20 hours at 1000C. Figure 9(a) has a bimodal distribution of cuboidal Ni<sub>3</sub>Al particles, with the larger particles on the order of 200 to 400 nm in edge length and the smaller particles an order of magnitude smaller in size. Other regions of the same multilayer thin film show coarsened regions as large as 2microns in size along with strings of Ni<sub>3</sub>Al particles that

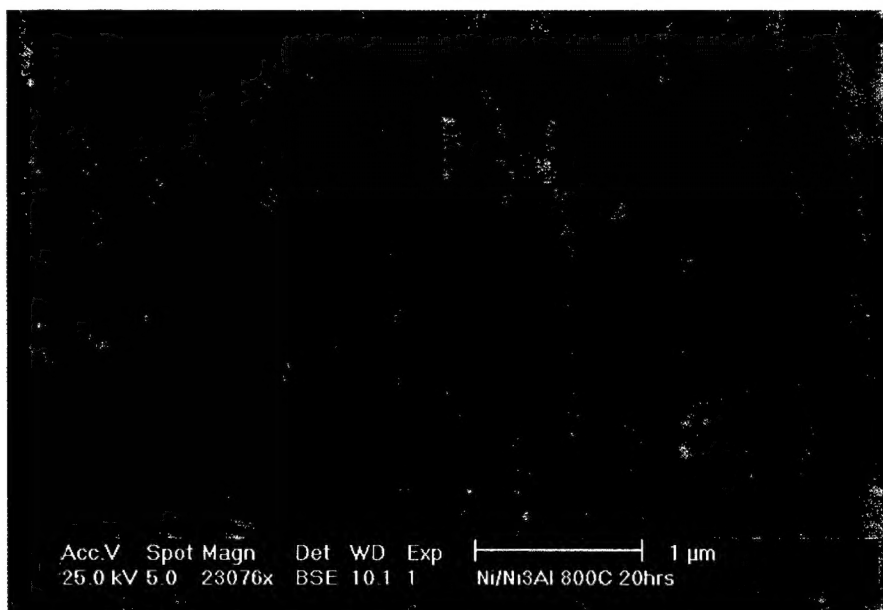


Fig. 7: Morphology of <001> 120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 800C for 20 hours (from Denman presentation).



are the remains of prior  $\text{Ni}_3\text{Al}$  layers. The morphology after 20 hours at 1100C (Fig. 10) shows an even larger density of  $\text{Ni}_3\text{Al}$  precipitates than at 1000C (Fig. 9a). The cuboidal morphology is well developed and displays a strong (001) epitaxy to the surrounding Ni(Al) matrix. The clusters of particles with a common orientation indicate that the thin film is polycrystalline with matrix grain sizes that are a large fraction of the total thin film thickness.

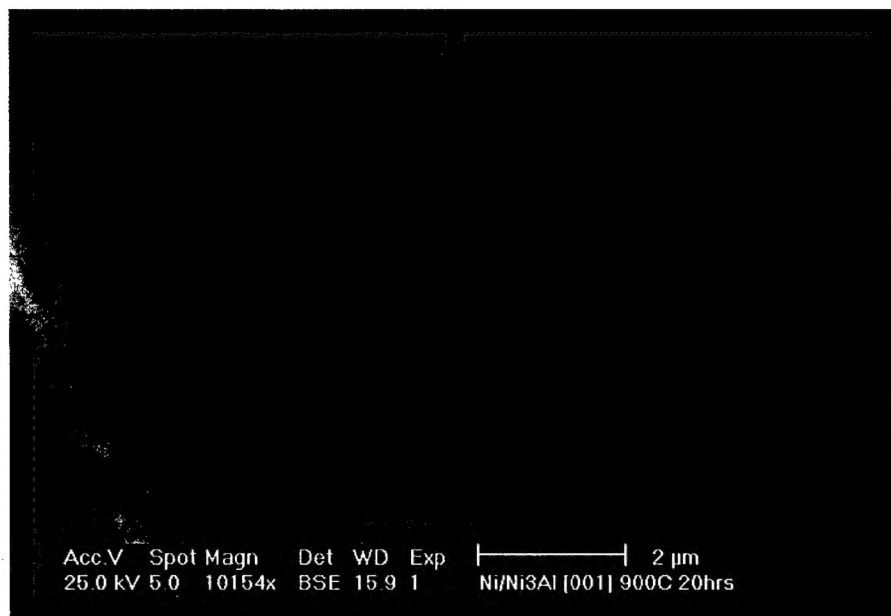


Fig. 8: Morphology of a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ - $\text{Ni}_3\text{Al}$  multilayer after heating to 900C for 20 hours in an Argon environment and cooling to room temperature (from Denman presentation).

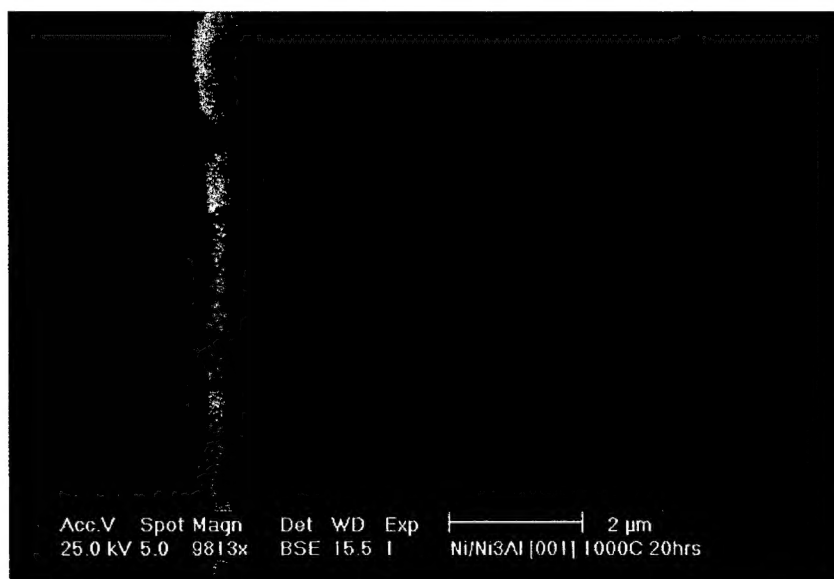


Fig. 9(a)

Fig. 9(a): See caption below.

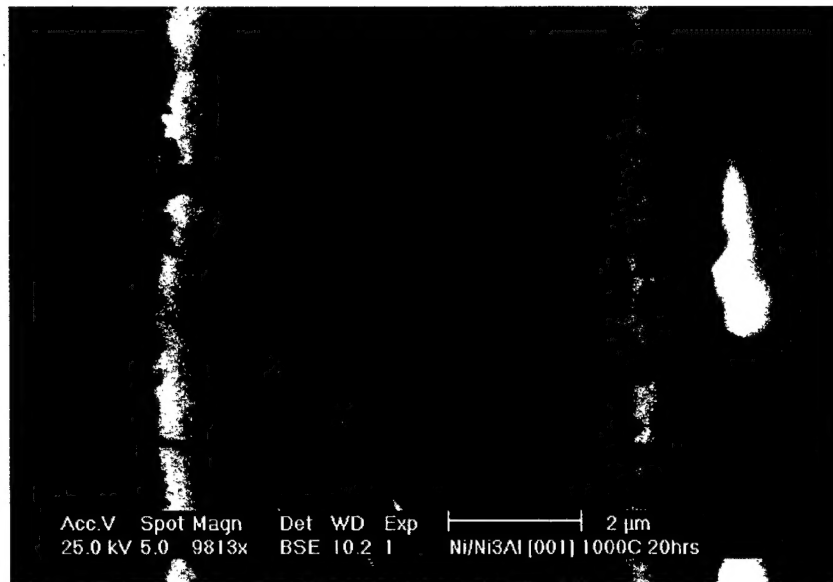


Fig. 9(b).

Fig. 9: Two distinct morphologies (a) and (b) observed in a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 1000C for 20 hours in an Argon environment and cooling to room temperature (from Denman presentation).

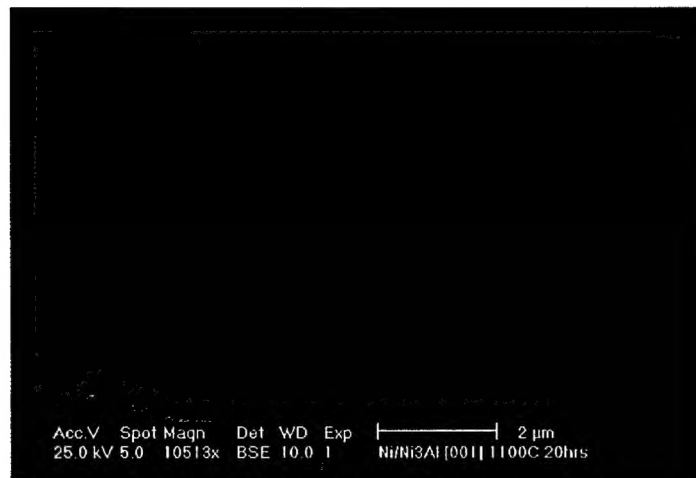


Fig. 10: Morphology observed in a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 1100C for 20 hours in an Argon environment and cooling to room temperature (from Denman presentation).

Effect of Heating Time and Cooling Conditions on the Morphology of 120nm/120nm Ni(Al)/Ni<sub>3</sub>Al Multilayer Thin Films with  $\langle 001 \rangle$  Texture

The motivation for this study stemmed from the observation that the bi-modal distribution of particles observed for the 1100C heat treatment (Fig. 10) may be due to

the solutionizing and precipitation of the  $\gamma'$ -Ni<sub>3</sub>Al phase, rather than simply a change in shape of the  $\gamma'$ -Ni<sub>3</sub>Al phase. **Figures 11, 12, and 13** show the resulting morphologies for 120nm/120nm Ni(Al)/Ni<sub>3</sub>Al multilayers with  $\langle 001 \rangle$  texture that were heated to 1100C for 5 hours, 10 hours, and 20 hours, respectively. The 5 hour sample was air cooled and the 10 and 20 hour samples were furnace cooled. Figure 11 provides strong evidence that these multilayered samples are solutionized after 5 hours at 1100C. It appears that solutionizing in these multilayers occurs at least 100C below the solutionizing temperature indicated in the Ni-Al phase diagram (**Fig. 19**). In particular, our Ni(Al) target was selected to have a composition of about 87at% Ni, so that the volume fraction of the Ni(Al) phase would be approximately 50% at 800C, based on the Ni-Al phase diagram. In that case, the temperature for solutionizing is predicted to be at least 1200C, compared to the solutionizing observed here at 1100C. The decrease in solutionizing temperature in strained multilayer thin films is consistent with the expectation that large strain energy densities associated with strain layer epitaxy and the numerous interfaces and grain boundaries can shift the temperature for phase transformations [1].

Figures 12 and 13 show the effect of holding the  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayers for 10 and 20 hours, respectively, in an Argon environment and then cooling slowly in the furnace. Neither case shows remnants of any of the layers in the as-sputtered structure. Rather, one observes a bi-modal distribution of cuboidal  $\gamma'$ -Ni<sub>3</sub>Al particles that is characteristic of slower cooling from a solutionized system. The distribution and volume fraction of  $\gamma'$ -Ni<sub>3</sub>Al particles appears to be more uniform for the 20 hour case, and suggests that there are differences in the uniformity of composition after holding the sample at 10 hours versus 20 hours at 1100C.

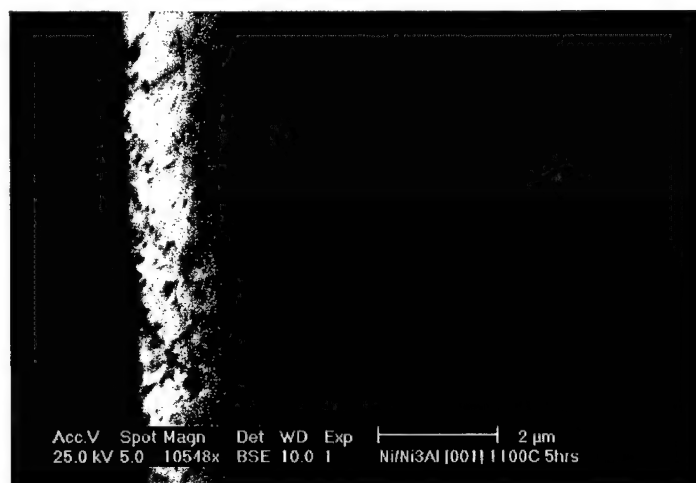


Fig. 9(b).

**Fig. 11:** Observed morphology of a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 1100C for 5 hours in an Argon atmosphere, then air cooling (from Denman presentation).

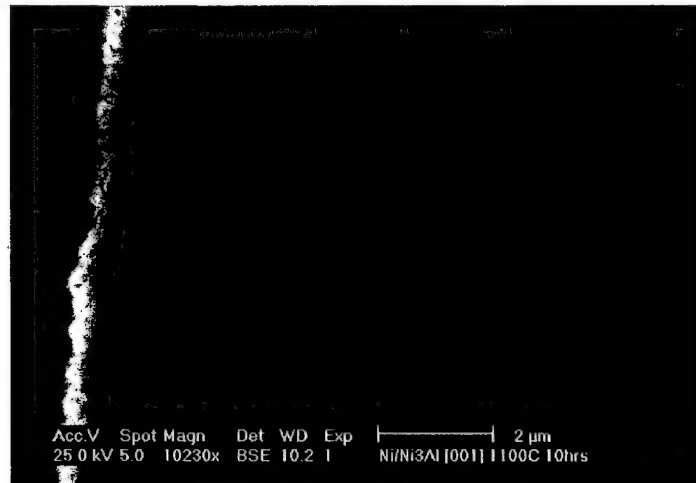


Fig. 12: Observed morphology of a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 1100C for 10 hours in an Argon atmosphere, then furnace cooled (from Derman presentation).

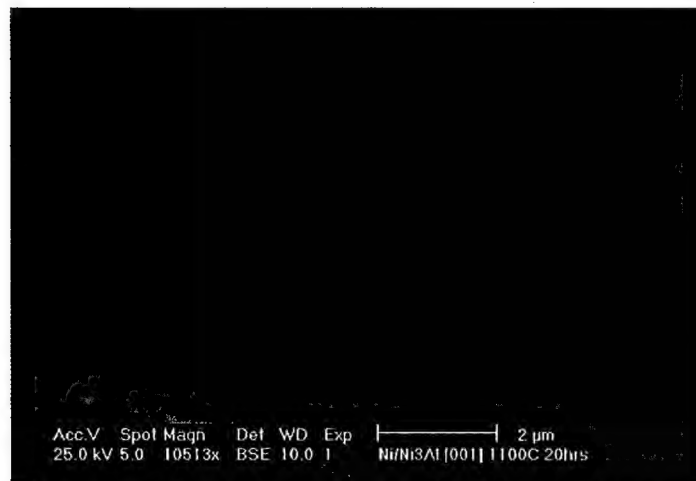


Fig. 13: Observed morphology of a  $\langle 001 \rangle$  120nm/120nm  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayer after heating to 1100C for 20 hours in an Argon atmosphere, then furnace cooled (from Derman presentation).

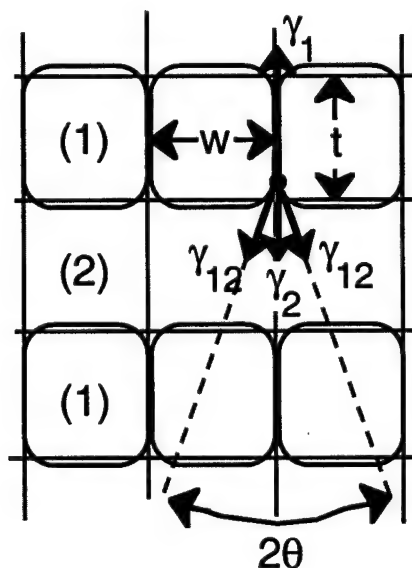
### Modeling Layer Breakdown based on Minimization of Interfacial and Grain Boundary Energies

It is well known that capillary forces affect the shape of a liquid vapor surface and the wetting of a solid by a liquid, by serving to minimize the excess free energy of the relevant liquid-vapor or liquid-solid interfaces. The same principles apply to a solid-solid interface and they have been used to determine conditions for the stability of multilayered materials [2, 3]. The concept is that the morphology of a laminate will evolve toward a geometry that minimizes the sum of interfacial grain boundary free energies. However, this approach neglects the elastic energy changes associated with redistribution of phases in systems with misfit/thermal strains or an applied macroscopic strain. The rationale proposed for neglecting these terms is that diffusional flow at elevated temperatures will serve to reduce elastic energy over time.

The layer geometry shown in Fig. 14 is considered relevant to modeling multilayered samples. It assumes that columnar grains within a layer are stacked on top of one another. Prior to any elevated temperature excursion, each layer may be thought of as an array of square prisms with in-plane width  $w$  and height  $t$ . Thus, Fig. 14 is only a two-dimensional cross section of the structure. Upon heating, there will be a tendency to reduce area defect content and the layer with the larger grain boundary energy (layer type 1 in Fig. 14) will begin to pinch off. A basic equilibrium condition for the node shown in Fig. 14 is

$$2\gamma_{12} \cos\theta + \gamma_2 - \gamma_1 = 0 \quad (1)$$

where  $\gamma_{12}$ ,  $\gamma_2$ , and  $\gamma_1$  are the energies per unit area of the interface, grain boundary in phase 2, and grain boundary in phase 1, respectively.



**Fig. 14.** Schematic of the energetic grain boundary and interfacial forces tending to pinch off layers [4].

The stability issue amounts to determining the critical depth to which a groove will penetrate into layer type 1 before the equilibrium grooving angle  $\theta$  is reached. To do so, the areas of interfaces and grain boundaries are varied to reach a minimum in area defect energy, subject to the constraint that the volume of a grain cannot change. The analysis predicts a critical initial aspect ratio,  $t/w$ , of columnar grains, below which the layer will pinch off. Clearly, stable multilayers are more likely when the magnitude of  $(\gamma_1 - \gamma_2)/2\gamma_{12}$  is small. If this ratio exceeds 1, then there is no equilibrium  $\theta$  possible and instability is predicted for all  $t/w$ . In the limit of  $(\gamma_1 - \gamma_2)/2\gamma_{12} = 0$ , multilayers with any  $t/w$  are predicted to be stable and for  $(\gamma_1 - \gamma_2)/2\gamma_{12} \geq 1$ , no multilayers are predicted to be stable.

Another geometry (not shown), with staggered placement of columnar grains in one layer relative to another, introduces a different mode of instability in which both layer types may pinch off. Although this geometry is not expected in as-deposited samples, grain boundaries may migrate to this staggered configuration at elevated temperature. The driving force to do so occurs since the area of the lower energy grain boundary (assumed to be  $\gamma_2$  in Fig. 14) can be reduced significantly if the staggered geometry is adopted. The limiting scenarios for the staggered geometry are that all  $t/w$  are stable when  $\gamma_1/2\gamma_{12}$  and  $\gamma_2/2\gamma_{12}$  approach 0, and no values of  $t/w$  are stable when either  $\gamma_1/2\gamma_{12}$  or  $\gamma_2/2\gamma_{12}$  approach or exceed 1.

Table I: Grain Boundary and Interfacial Energies in  $\text{mJ/m}^2$

Quantity	Exper.	Theor.	Value used in Fig. 15
$\gamma_{\text{gb}}(\text{Ni})$	866 [5]	1210 [6]	
$\gamma_{\text{gb}}(\text{Al})$	325 [5]		
$\gamma_{\text{gb}}(\text{Ni}(\text{Al}))$			866
$\gamma'_{\text{gb}}(\text{Ni}_3\text{Al})$		1260 [6]	902
$\gamma_{\gamma/\gamma'}$ interface	10-20 [7] 200[8]		

Prediction of Stability for  $\gamma\text{-Ni}(\text{Al})/\gamma'\text{-Ni}_3\text{Al}$  Multilayers based on Minimization of Grain Boundary and Interfacial Energies

Figure 15 shows the predictions of the Josell theory to  $\gamma\text{-Ni}(\text{Al})/\gamma'\text{-Ni}_3\text{Al}$  multilayers. Regions of stability and instability to pinching off of  $\gamma'(\text{Ni}_3\text{Al})$  layers are shown as a function of columnar grain aspect ratio and energy of the  $\gamma/\gamma'$  interface. The plot is based on estimates of  $866 \text{ mJ/m}^2$  for a  $\gamma\text{-Ni}(\text{Al})$  grain boundary and  $902 \text{ mJ/m}^2$  for a  $\text{Ni}_3\text{Al}$  grain boundary. They are obtained using both experimental measurements and theoretical predictions of grain boundary energies as summarized in Table I. There are no experimental or theoretical values for  $\gamma_{\text{gb}}(\text{Ni}(\text{Al}))$ . However, estimates for  $\gamma_{\text{gb}}(\text{Ni})$  range from an experimental value of  $866 \text{ mJ/m}^2$  to a theoretical value of  $1210 \text{ mJ/m}^2$ . We approximate  $\gamma_{\text{gb}}(\text{Ni}(\text{Al})) \approx \gamma_{\text{gb}}(\text{Ni}) = 866 \text{ mJ/m}^2$ , and use the experimental value since the theoretical estimate appears to be an overestimate [9]. A corresponding value  $\gamma'_{\text{gb}}(\text{Ni}_3\text{Al}) = 902 \text{ mJ/m}^2$  is adopted in Fig. 4, based on the observation that the theoretical value of  $\gamma'_{\text{gb}}(\text{Ni}_3\text{Al})$  in Table I is approximately 4% larger than the theoretical value of  $\gamma_{\text{gb}}(\text{Ni})$ .

The stable versus unstable nature of  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayers depends on the value of interfacial energy. The most striking effect is that estimates of interfacial energy reported in Table I range from (10 to 20) mJ/m<sup>2</sup> for coherent <001> interfaces in  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al superalloys with cuboidal particles (e.g., see Fig. 20a) to 200 mJ/m<sup>2</sup> for semicoherent interfaces in rafted  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al structures (e.g., see Fig. 20b). Thus, the stability diagram in Fig. 15 predicts that if interfaces are semicoherent, then  $\gamma/\gamma'$  multilayers with grain boundary aspect ratios  $t/w > 0.1$  would be *stable*. For comparison, multilayers with coherent interfaces, with  $\gamma_{\gamma/\gamma'}$  interface  $\sim 20$  mJ/m<sup>2</sup>, are predicted to be *unstable* for all  $t/w$  shown.

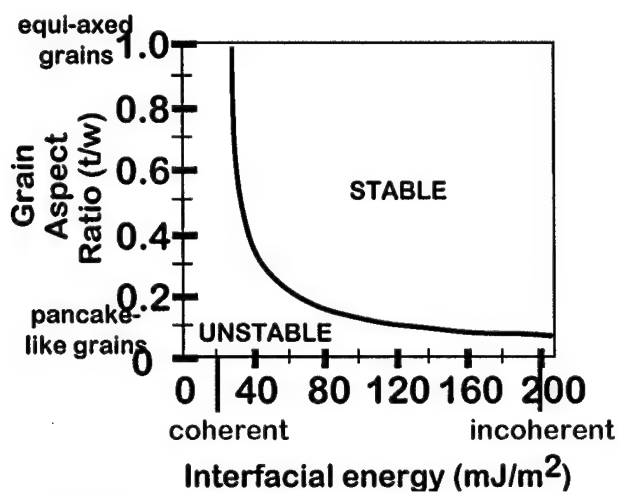


Fig. 15: Stability diagram for pinching off of  $\gamma'$ -Ni<sub>3</sub>Al layers in  $\gamma$ -Ni(Al)/ $\gamma'$ -Ni<sub>3</sub>Al multilayered samples, based on columnar grain boundary energies of 866 and 902 mJ/m<sup>2</sup> for  $\gamma$ -Ni(Al) and  $\gamma'$ -Ni<sub>3</sub>Al layers, respectively.

#### Modeling Layer Breakdown based on Minimization of Interfacial and Elastic Strain Energies

Sridhar et al. [10] consider instability of multilayers based on the computation of the elastic energy and interfacial energy of multilayered systems which are perturbed from a flat interfacial morphology. The analysis includes the change in elastic energy of layered structures with elastic misfit between layers but neglects the contribution from changes in energy of columnar grain boundaries. Stability for multilayered systems is described in terms of the misfit strain  $\epsilon^*$ , mismatch  $\alpha = (E_1 - E_2)/(E_1 + E_2)$  in Young's moduli of the two alternating layer types in the multilayer, and volume fraction  $f$  of layer type 1. **Figure 16** shows the stability predictions for a multilayer of alternating layer types 1 and 2, with equal layer thickness ( $f = 0.5$ ). The vertical axis is the ratio of the isotropic eigenstrain (i.e., misfit strain) in phase 1 divided by the in-plane macroscopic strain on the multilayer. The horizontal axis is the elastic mismatch. Regions in which a flat interface is predicted to be stable are shaded and marked with an "s". Over a large range of applied tensile strain, the layered morphology is stable provided the elastically stiffer phase has a positive eigenstrain. Equivalently, stability is predicted when the elastically softer phase has a negative eigenstrain. In the absence of any macroscopic

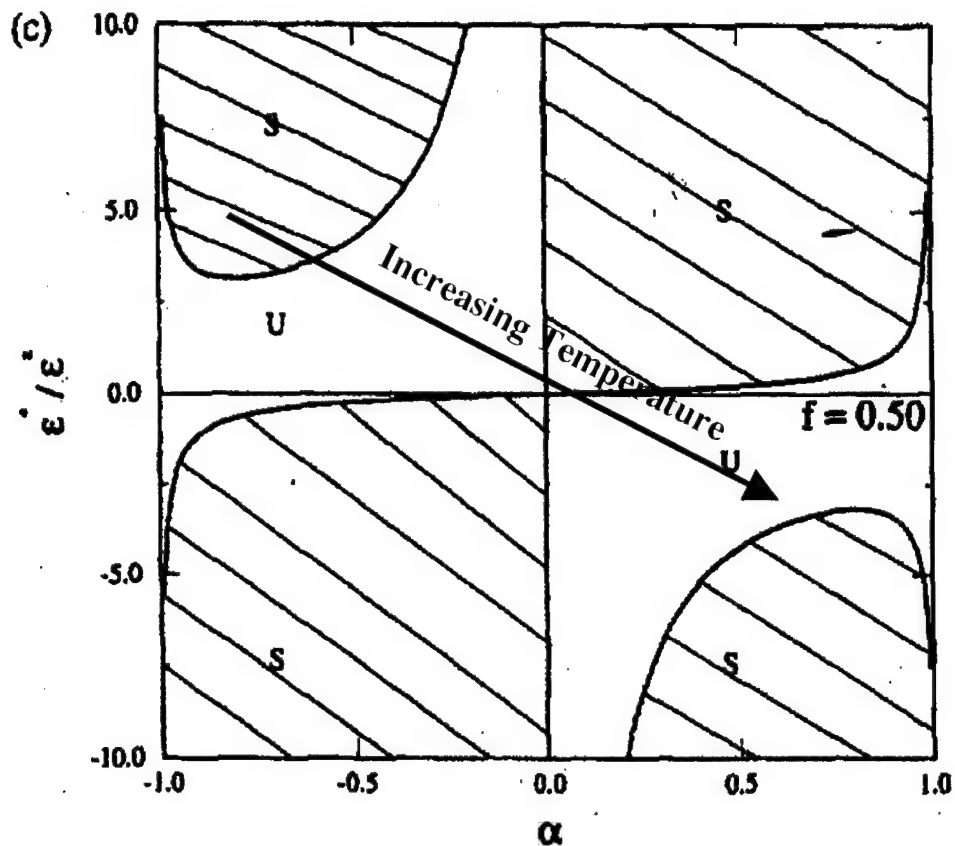


Fig. 16: Stability diagram for pinching off of  $\gamma'$ - $\text{Ni}_3\text{Al}$  layers in  $\gamma\text{-Ni(Al)}/\gamma'\text{-Ni}_3\text{Al}$  multilayered samples, based on application of a model by Sridhar et al. [10].

applied strain, the ordinate goes to  $\pm$  infinity and stability is predicted for all combinations of elastic mismatch and eigenstrain.

Prediction of Stability for  $\gamma\text{-Ni(Al)}/\gamma'\text{-Ni}_3\text{Al}$  Multilayers based on Minimization of Interfacial and Elastic Energies

The stability diagram in Fig. 16 requires information about the eigenstrain, modulus mismatch, and volume fraction of the multilayer system. All of these quantities are expected to change with temperature. In particular, Fig. 17 shows the evolution of lattice parameter with temperature for the  $\gamma$  and  $\gamma'$  phases. Based on the information for the [001] direction, the  $\gamma'$  phase is predicted to have the larger lattice parameter below approximately 800°C, and the reverse is true above 800°C. Thus, if the  $\gamma'$  phase is taken to be the "1" phase in Fig. 16, then the eigenstrain is positive.

Information about the evolution of Young's modulus with temperature is shown in Fig. 18. In particular, Ni has a larger elastic modulus below approximately 600°C and the reverse is true for  $T > 600^\circ\text{C}$ . Therefore, the mismatch parameter  $\alpha$  is expected to be negative at room temperature and to reverse sign at 600°C.



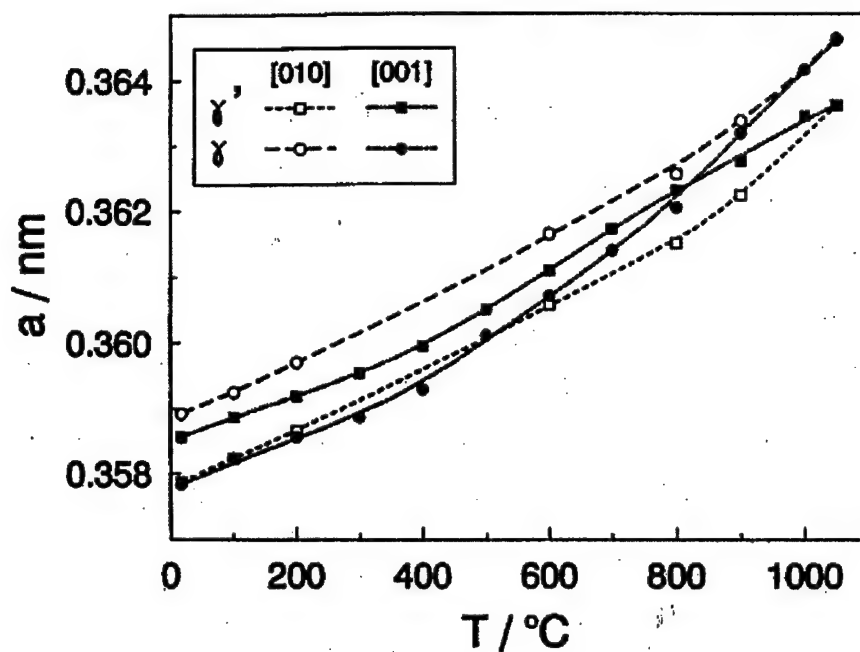


Fig. 17: Stress-free lattice parameters of  $\gamma$ -Ni(Al) and  $\gamma'$ -Ni<sub>3</sub>Al phases as a function of temperature [11].

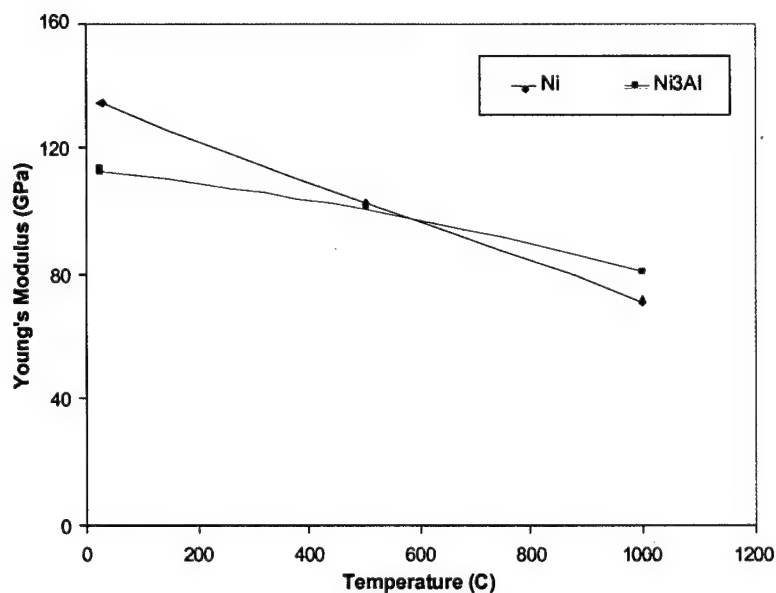


Fig. 18: Young's moduli of  $\gamma$ -Ni(Al) and  $\gamma'$ -Ni<sub>3</sub>Al phases as a function of temperature [12].

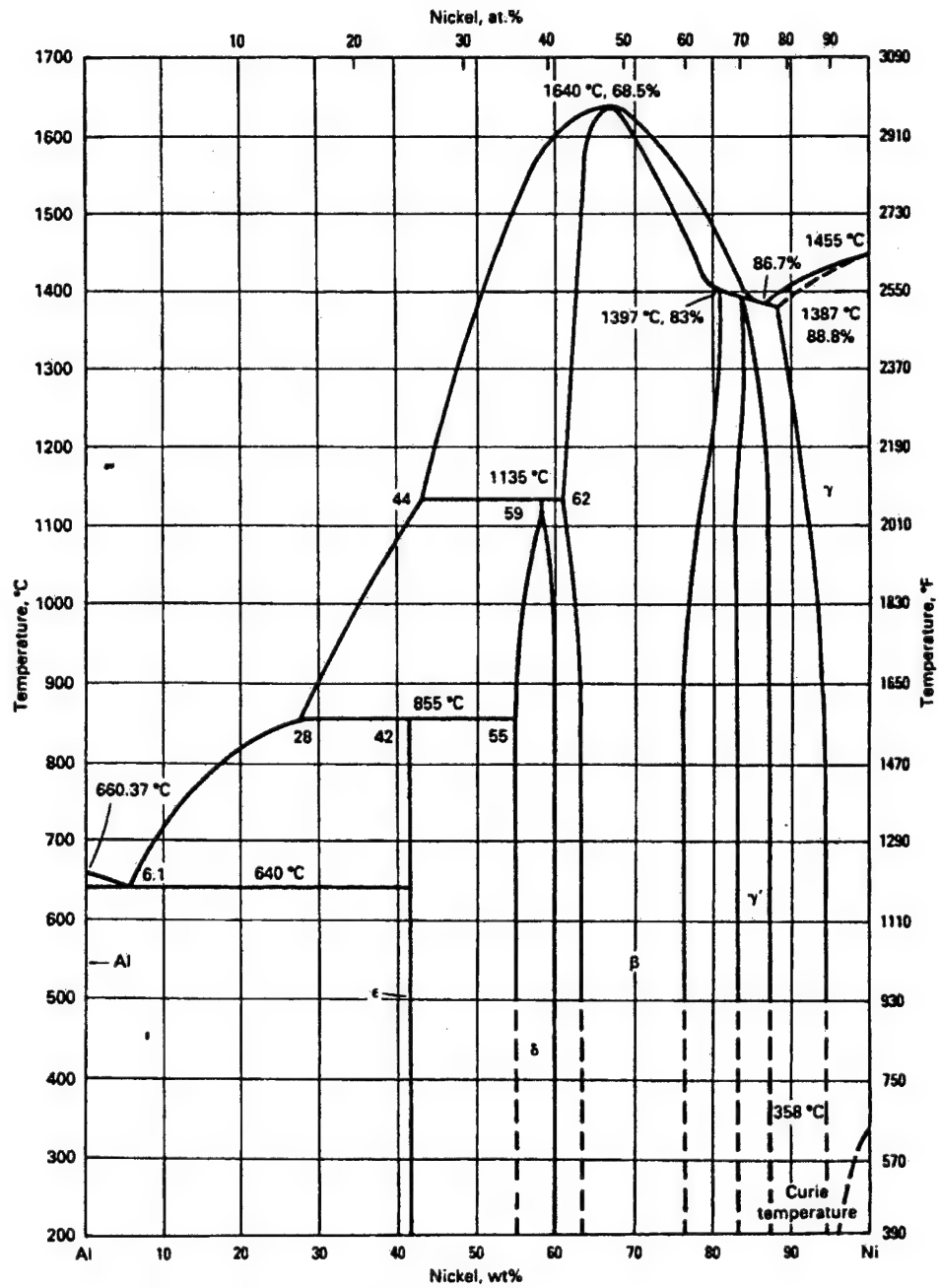


Fig. 19: Ni-Al phase diagram [13].

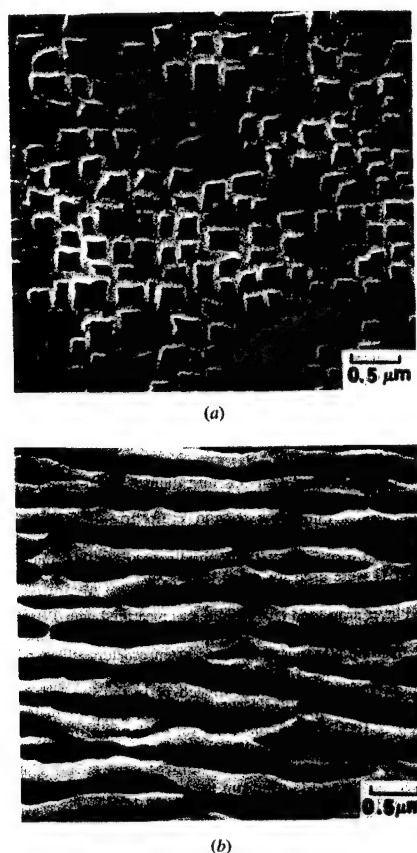


Fig. 20: NASAIR 100, a commercial Ni-base gamma/gammaprime alloy (a) as produced and (b) after 100 hours at 1000C and 140MPa tension [14].

Finally, the phase diagram information in Fig. 19 shows that the equilibrium volume fraction of  $\gamma'$  is predicted to decrease with increasing temperature. Thus, the stability plot for  $f = 0.5$  in Fig. 16 is only valid at a specific temperature and results for smaller values of  $f$  should be used as the temperature is increased.

Based on the information in Figs. 17-19, a line as shown in Fig. 16 can be constructed to indicate the stability of a  $\gamma/\gamma'$  multilayer with increasing temperature. At smaller temperature, the stability of a multilayer under a small tensile strain is determined by the portion of the line in the upper left-hand quadrant of the diagram. There, stability is predicted provided the tensile strain is not more than approximately 40% of the eigenstrain. At approximately 600C, the line is predicted to cross from the upper-left to the upper-right quadrant, where stability is predicted also. At 800C, the line is predicted to cross from the upper-right to the lower-right quadrant and become unstable. At even larger temperatures, the multilayers may or may not be stable, depending on whether the stability region in the lower-right quadrant can be reached. Stability maps for smaller volume fraction show that this stability region shrinks with decreasing volume fraction,  $f$ , of phase 1 ( $\gamma'$ ), so that at  $f = 0.25$ , the lower right-hand portion of the line is unlikely to be in a stable region. Thus, predictions based on elastic and interfacial energy suggest the

multilayer will move between stable and unstable regions as the temperature and applied strain is varied.

Based on this model, an increase in applied macroscopic strain will decrease the slope of the stability line drawn in Fig. 16. This slope decrease would increase the temperature range over which the multilayer is unstable in the upper-left and lower-right quadrants.

## Conclusions

Multilayers consisting of alternating 20nm/20nm and 120nm/120nm layers of  $\gamma$ -Ni(Al) and  $\gamma'$ -Ni<sub>3</sub>Al appear to be inherently unstable to pinching off of  $\gamma'$ -Ni<sub>3</sub>Al layers when held at 800C for 100 hours. However, the rate at which pinching off occurs is larger for 20nm/20nm than for 120nm/120nm layer thickness, and much larger for samples with  $\langle 111 \rangle$  compared to  $\langle 001 \rangle$  crystal orientation to the interface normal. Additional testing on  $\langle 001 \rangle$  120nm/120nm layers indicates that the layers are also unstable at 900C, 1000C, and 1100C. A surprising result is that solutionizing of the multilayers occurs at 1100C, which is at least 100C lower than that predicted by the Ni-Al phase diagram (Fig. 19).

Two models are discussed to help understand the instability and to identify regimes in which the multilayered structure may be stable. The Josell model is based on a trade-off of interfacial and grain boundary energies and it predicts that  $\langle 001 \rangle$  multilayers with 120nm/120nm thickness should be stable while 20nm/20nm should not be stable, due to the large difference in interfacial energy expected for coherent versus semi-coherent interfaces. An important feature of this model is that multilayers with needle-like columnar grains should be more stable than pancake type grains.

The Sridhar et al. model considers the trade-off in interfacial energy and elastic energy. The latter is due to mismatch in lattice parameter, mismatch in elastic moduli, and application of a remote in-plane strain. Based on a survey of changing lattice parameters, elastic moduli, and equilibrium volume fraction with temperature and their insertion into the model, the prediction is that  $\gamma/\gamma'$  multilayers should be stable at low temperature and become unstable in the vicinity of 600C. The multilayers are then predicted to be stable between 600 and 800C, beyond which they are unstable to at least 1000C.

Neither model appears to capture all of the relevant features needed to understand stability in this system. The Josell model documents the geometric advantages that needle-like grains provide in suppressing grooving but does not contain information about the effect of elastic energy. Conversely, the Sridhar et al. model contains no information about columnar grain boundary structure but it does incorporate elastic energy.

Future work is suggested in the following areas. First, the stability of stressed multilayers should be studied at varying temperatures and stress magnitudes. It is well known that stress at elevated temperatures can induce rafting, in which a cuboidal microstructure changes into a layered morphology, as shown in Fig. 20. Neither of the existing models reviewed here has the capacity to explain the stability of the layered microstructure under an applied stress. Thus, the second suggested effort is to adopt a numerical simulation of the stability process, via a phase-field approach, for example, to

more accurately predict the features of a multilayered structure with columnar grain boundaries. Finally, an important experimental avenue to pursue is the deposition of a third phase or element at interfaces, which will serve to pin interfaces and slow down the process of thermal grooving.

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Hamish L. Fraser	Professor, Ohio State University
Gregory Thompson	Graduate Student, Ohio State University
Jason Fain	Graduate Student, Ohio State University

#### Publications (as pertaining only to this AASERT grant and not the parent project)

G.B. Thompson, R. Banerjee, X.D. Zhang, P.M. Anderson, and H.L. Fraser, "Chemical Ordering and Texture in Sputter-deposited Ni<sub>3</sub>Al Thin Films", *to appear in Acta mater.* in 2001.

R. Banerjee, J.P. Fain, P.M. Anderson, and H.L. Fraser, "Influence of Crystallographic Orientation and Layer Thickness on the Fracture Behavior of Ni/Ni<sub>3</sub>Al Multilayered Thin Films", *Scripta Mater.* **44**, 2629 (2001).

Banerjee, R., Fain, J.P., Anderson, P.M., and Fraser, H.L., "Processing, Microstructure, and Fracture Behavior of Nickel/Nickel Aluminide Multilayered Thin Films", **Mater. Res. Soc. Symp. Proc. 594**, Warrendale, PA (1999). pp. 19-24.

J.P. Fain, R. Banerjee, D. Josell, P.M. Anderson, H. Fraser, N. Tymiak, and W. Gerberich, "Morphological Stability of Ni(Al)/Ni<sub>3</sub>Al Nanolaminate Composites", in **MRS Symp. Proc. 581**, MRS, Warrendale, PA (1999).

### **Interactions/Transitions**

#### **a. Participation/presentations at meetings, conferences, seminars:**

- Sperling, E., and Anderson, P.M., "Thermal Stability of Nanoscale Multilayers", Denman Graduate Research Forum, Ohio State University, May 21, 2001.
- Anderson, P.M., "Computer Modeling of Crystal Slip and Diffusional Transport in Polycrystals," Plasticity Workshop, UES, Inc., Dec. 6, 2000.
- Anderson, P.M., "Design of Multilayer Thin Films for Optimal Strength", Brown University Joint Materials/Solid Mechanics Seminar, Dec. 4, 2000.
- Anderson, P.M. and Li, Z., "The Ultimate Strength in Multilayer Thin Films", MRS Symp on The Limits of Strength in Theory and Practice, MRS Fall Meeting, November 29, 2000.
- Anderson, P.M. and Foecke, T., "Deformation Mechanisms in Single Crystal Metallic Nanolaminates: Theory and Experiment", MRS Symp on Structure and Mechanical Properties of Nanophase Materials--Theory and Computer Simulations vs Experiment, MRS Fall Meeting, November 29, 2000.
- Anderson, P.M., "Deformation Mechanisms in Multilayered Materials", AFOSR Metallic Materials Meeting, St. Louis, MO, Oct. 12, 2000,
- Anderson, P.M. and Li, Z., "A Peierls Analysis of the Critical Stress for Transmission of a Screw Dislocation Across a Coherent, Sliding Interface", International Conference on Strength of Materials, Asilomar, CA, Aug. 29, 2000.
- Anderson, P.M., "Design of Multilayer Thin Films for Optimal Strength", Center for Materials Research, Ohio State University, May 18, 2000.
- Fain, Jason P., Banerjee, R., Josell, D., Anderson, P.M., Fraser, H., Tymiak, N., Gerberich, W.W., "Morphological Stability of Ni(Al)/Ni<sub>3</sub>Al Nanolaminate Composites", MRS Fall Meeting, Nov. 29-Dec. 3, 1999, Boston, MA.
- Banerjee, R., Fain, J.P., Anderson, P.M., and Fraser, H.L., "Processing, Microstructure, and Fracture Behavior of Nickel/Nickel Aluminide Multilayered Thin Films", , MRS Fall Meeting, Nov. 29-Dec. 3, 1999, Boston, MA.
- Anderson, P.M., Rao, S., Cheng, Y., and Hazzledine, P.M., "The Critical Stress for Transmission of a Dislocation Across An Interface: Results from Peierls and Embedded Atom Models", MRS Fall Meeting, Nov. 29-Dec. 3, 1999, Boston, MA.
- Anderson, P.M., "Deformation and Fracture in Nanolaminated Metallic/Intermetallic Materials, Case Western Reserve University, March 16, 1999.
- Anderson, P.M., Fraser, H.L., Foecke, T., Josell, D., "Deformation and Fracture of Intermetallic Materials," AFOSR Metallic Materials Contractor's Meeting, San Diego, CA, 4-5 March, 1999.

- Xin, X.J., Cheng, Y., and Anderson, P.M., "Dislocation Transmission Through a Bimaterial Interface based on Peierls Dislocation Model, 1998 TMS Fall Meeting, October 12-15, 1998, Rosemont, IL.
- Anderson, P.M., Muju, S., and Mendelsohn, D., Modeling of Microcrack Toughening in Two-Phase Multilayered Media, , 1998 TMS Fall Meeting, October 12-15, 1998, Rosemont, IL.
- Anderson, P.M. and Foecke, T., Slip Propagation in Metallic Multilayered Thin Films, , 1998 TMS Fall Meeting, October 12-15, 1998, Rosemont, IL.
- P.M. Anderson, "Deformation in Nanoscale Layered Metallic Materials," Workshop on properties of ultrafine layered materials, Los Alamos National Labs, April 5, 1998.
- P.M. Anderson and E.R. Kreidler, Jr., "Dislocation-based models of stress-strain behavior in multilayered thin films," MRS Fall '97 Meeting, Boston, MA. Dec. 4, 1997.
- P.M. Anderson, Computer-based Interactive Modules using MathCad," MRS Fall '97 Meeting, Boston, MA. Dec. 4, 1997.
- H.L. Fraser, "Interface Properties and Phase Stabilities in Metallic Multilayers", TMS Fall Meeting, Indianapolis, September 1997.
- H.L. Fraser, "Structural Stabilities in Intermetallic Compounds and Multilayered Materials", Purdue University, October, 1997
- H.L. Fraser, "Structural Stabilities in Multilayered Materials", Göttingen, October 1997.
- H.L. Fraser, "Ductility, Toughness and Structural Stabilities in Intermetallics and Multilayered Materials", Cambridge University, Cambridge, UK, November 1997
- H.L. Fraser, "Processing and Properties of Advanced Nb-based Intermetallics", PFAMVI, Singapore, November 1997.
- H.L. Fraser, "Strengthening and Toughening Issues in Nb-Ti Based Intermetallics", TMS Annual Meeting, San Antonio, February, 1998.
- H.L. Fraser, "The Interchange between Experimental and Computational Efforts in the Accelerated Maturation of Materials", Mardi Gras Conference, Baton Rouge, LA, February 1998.
- H.L. Fraser, "Microstructure and Mechanical Behavior of Nb Aluminides", 3rd. International Workshop on Ordered Intermetallic Alloys and Composites, HangZhou, PRC, April 1998.
- H.L. Fraser, "Ordering, Deformation Mechanisms, and Oxidation of B2 Nb-based Aluminides", Kyoto Workshop on High-Temperature Intermetallics, Kyoto, Japan, May 1998.
- H.L. Fraser, "Understanding Alloying Addirions to TiAl", Workshop on TiAl, COST 513, Neuchâtel, Switzerland, June 1998.
- H.L. Fraser, "Co-Continuous Ceramic Composites", Robert Bosch Company, Stuttgart, Germany, July 1998.

**b. Consultive and Advisory Functions to Other Labs/Agencies:**

-Dr. Fraser has served on the Materials and Structures Panel of the USAF Scientific Advisory Board, involving reviewing of the Materials and Structures programs of AFOSR and Materials Directorate of Wright Facility, Materials Directorate (WL/ML). He has also consulted for the Characterization Facility, Materials Directorate (WL/ML). Dr. Anderson has continued to serve as a reviewer of proposals for DOD and NSF

Agencies and interacts on multilayered systems with Dr. P. Hazzledine at UES, Inc., and Drs. Tim Foecke and Dan Josell at NIST.

**Awards Received**

Presented two invited presentations at the Fall 2000 MRS Meeting that were based on AFOSR funded work.

**Transitions**

none